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New Catalytic Routes to Preceramic Polymers: Ceramic Precursors
to Silicon Nitride and Silicon-Carbide Nitride

by

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NEW CATALYTIC ROUTES TO PRECERAMIC POLYMERS: CERAMIC PRECURSORS TO SILICON NITRIDE AND SILICON-CARBIDE NITRIDE

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ABSTRACT.

Pyrolyses of a set of silicon and nitrogen substituted polysilazanes are conducted under a set of standard conditions (5°C/min to 900°C in a nitrogen atmosphere). The apparent ceramic compositions and ceramic yields for pyrolyzed samples of the polysilazanes $-\text{[Ph(II)SiNH]}_x-$, $-\text{[C}_6\text{H}_{13}\text{(II)SiNH]}_x-$, $-\text{[Me(II)SiNH]}_x-$, and $-\text{[H}_2\text{SiNMe]}_x-$ are determined. Preliminary conclusions concerning structure/reactivity relationships are discussed based on the pyrolysis results.

INTRODUCTION

The potential utility of organometallic oligomers and polymers as low temperature precursors to advanced ceramic materials has recently generated considerable interest [1] in the synthesis of preceramics for numerous materials including silicon carbide (SiC) [2, 3], silicon nitride (Si₃N₄) [3, 4], aluminum nitride (AlN) [5], and boron nitride (BN) [6, 7], as well as precursors for many of the refractory metals (e.g., WC [8], TiC [9], TiN [10]) and high T_c ceramic superconductors [11].

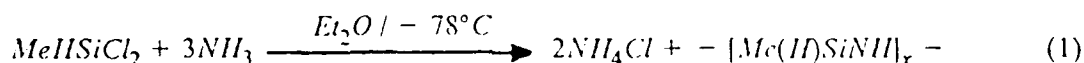
As with any new area of research, much of the work published to date has been Edisonian in nature. Because so little is known about the high temperature reaction chemistry of organometallics, it has not been possible to develop general principles for the design and synthesis of preceramics or for their selective pyrolytic transformation into high purity, high density, defect-free ceramic materials. Indeed, the very definition of "high temperature" has not been discussed. Because we observe "chemical reactivity" (e.g., evolution of discrete molecular species other than H₂) during the decomposition of preceramics in the range of 200-800°C, we use this range to define the "high temperature" chemistry regime.

A number of notable problems consistently arise in the search for a useful precursor to a given material. These problems include the need for: (1) a clean synthetic approach; (2) high ceramic yield; and (3) high selectivity to the target ceramic. The need for high ceramic yield

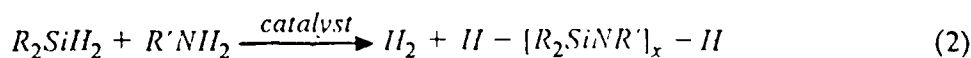
and high selectivity place considerable constraints on the types of synthetic approaches that can be used.

High ceramic yield is desirable because most precursors have relatively low densities (typically 1-2g/cc) compared with the resultant ceramic products (Si_3N_4 or $\text{SiC} \approx 3.2 \text{ g/cc}$). Thus, even if all of the precursor were transformed into ceramic product, a volume change of 60-70% would be required to obtain a fully dense SiC or Si_3N_4 ceramic product. If 50% of the mass of the preceramic were to be lost during pyrolysis, then the volume change to fully dense material could be 80-85%. These types of volume changes constrain the uses of preceramics to coating, fiber, and binder applications, where volume change is less important than what is required to form near-net shape, fully dense, three-dimensional pieces.

Low ceramic yields frequently result because the preceramic contains excessive amounts of extraneous ligands originally incorporated to provide tractability or stability to the organometallic. Efforts to reduce the number of extraneous ligands to improve the ceramic yield frequently result in a preceramic that is air and/or moisture sensitive or thermally labile. These parameters create the need for high yield, "clean" synthetic routes to preceramics, because the greater the effort required to purify a reactive preceramic, the more opportunity to incorporate additional impurities. Reaction 1 illustrates one of the standard routes to polysilazane precursors to Si_3N_4 .

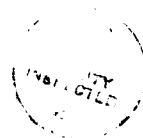


In this reaction, it is necessary to separate one mole of preceramic product from two moles of ammonium chloride. This reaction can be considered to be a "dirty" synthetic route because of the separation problems involved. Reaction (2), a dehydrocoupling reaction, illustrates a cleaner synthetic approach to polysilazane synthesis because the only by-product, H_2 , is a gas that can be removed readily.



A number of groups have now developed synthetic routes to preceramic compounds that are founded on the elimination of a volatile by-product such as H_2 [12], CH_4 [5], RNH_2 [10, 14], Me_3SiCl [3, 6]. This approach represents a useful solution to the problem of purification of labile organometallic precursors.

The problems of establishing what design parameters control selectivity to specific ceramic products has received much less attention. This is in part due to the lack of knowledge about the high temperature reaction chemistry of organometallics and in part because very few investigations have considered the effects of precursor structure on precursor reactivity and selectivity to ceramic products. The object of the work reported here represents initial studies on structure:reactivity patterns for a select set of silicon and nitrogen-substituted polysilazanes.



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RESULTS AND DISCUSSION

Table 1 lists typical ceramic yields and ceramic products for a set of structurally related polysilazanes pyrolyzed to 900°C under nitrogen at a 5°C/min heating rate, except for the H_2SiNMe polysilazanes, which were heated at 0.5°C/min. We find no differences in ceramic yield when heating rates are varied between 0.5°C and 10°C/min. The compositions are calculated using nitrogen content as the limiting elemental quantity, except in the case of the H_2SiNMe polysilazane where silicon is used.

Table 1. Ceramic Yields and Apparent Ceramic Composition for a Series of Si and N Substituted Polysilazanes Following Pyrolysis to 900°C Under N_2 at a Heating Rate of 5°C/min

Compound	Ceramic Yield (%)	Apparent Ceramic Composition ^a			
		Si_3N_4 %	SiC %	C(x's) %	N(x's) %
$-\text{[Ph(H or NH)SiNH]}_x-$	61	29	12	42	--
$[\text{C}_6\text{H}_{13}(\text{H or NH)SiNH}]_x-$	35	major product			
$-\text{[MeHSiNH]}_x - [\text{MeSiN}]_y-$ ^b	85	65	29	4	--
$-\text{[Me(H or NH)SiNH]}_x-$	57	64	25	10	--
$-\text{[H}_2\text{SiNMe]}_x[\text{H(NMe)SiNMe}]_y-$	63	75	--	18	6

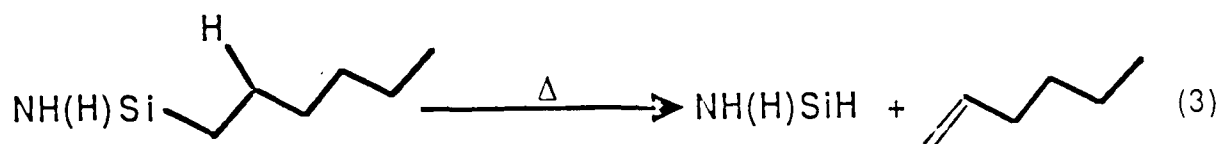
^aAll compositions are calculated based on the chemical analyses of the ceramic products. Because all the 900°C products are amorphous, these values may not actually represent the true ceramic compositions.

^bBased on the work of Seyferth and Wiseman [4b]. The actual preceramic has crosslinks between polymer chains. These crosslinks take the form of 1,3-diaza-2,4-silacyclobutane rings. A typical analysis found for a ceramic product is 59.52% Si, 26.07% N, 12.87% C [4c].

The results shown in Table 1 permit us to make some general observations concerning structure and reactivity. For example, the hexyl and phenyl polysilazane data permit a comparison of the effects of unsaturation and excess mass (in the preceramic) on the ceramic yield and composition. Excess is defined in terms of the ceramic yield expected if the only pyrolysis product is silicon nitride and/or SiC.

The silicon nitride ceramic yield expected for both the phenyl and hexyl polysilazanes is approximately 30%. We do observe a ceramic yield of ca. 35% for the hexyl polysilazane; however, pyrolysis of the phenyl silazane gives a 60+ % ceramic yield. Chemical analysis of the ceramic product from the hexyl polysilazane indicates that it is mainly Si_3N_4 with some carbon; whereas, the phenyl derivative results in a ceramic containing 29% Si_3N_4 , 12% SiC and 40+ % carbon.

Why do the hexyl polysilazane ceramic yield and composition differ so much from the phenyl polysilazane? We suspect that the hexyl polymer has an accessible decomposition pathway, β -elimination as shown below, which is not available to the phenyl polysilazane.



This would explain the very low carbon content observed in the hexyl pyrolysis product and the high relative yield of silicon nitride. The high carbon content found with the phenyl polysilazane indicates that the phenyl group is incorporated into the intermediate phase during heating rather than being ejected as a consequence of Si-phenyl bond homolysis or heterolysis.

One observation, suggested by the composition of the phenyl polysilazane ceramic product, concerns the effects of initial elemental stoichiometry on selectivity to ceramic product. If both polysilazanes are entirely linear, the Si:N stoichiometry in both polysilazanes will be 1:1. If all of the silicon is converted to Si_3N_4 , then the optimal Si:N stoichiometry should be closer to 0.75:1.0 to support the 3:4 stoichiometry required for silicon nitride; assuming all of the silicon and nitrogen in the precursor are incorporated in the final ceramic product. If there is insufficient nitrogen to balance the silicon in the preceramic, as would be the case for a 1:1 stoichiometry, then the silicon is available to form free silicon metal or silicon carbide in the ceramic pyrolysis product. If it were to form SiC, based on the stoichiometry arguments, the ratio of SiC to Si_3N_4 in the phenyl polysilazane ceramic product would be 1:3. Table 1 shows that the ratio is approximately 1:3 (12%:29%), suggesting that there is some effect of precursor stoichiometry on selectivity to specific ceramic products. More work will be required to quantify these effects; however, this idea receives further support from a comparison of the two types of MeSi polysilazanes (see below).

The hexyl and phenyl polysilazanes used in the pyrolysis studies listed in Table 1 were prepared under very mild conditions as shown in reactions (4) and (5), using a new method of catalyst preparation wherein the $\text{Ru}_3(\text{CO})_{12}$ is first heated with the silane prior to reaction with ammonia [15].

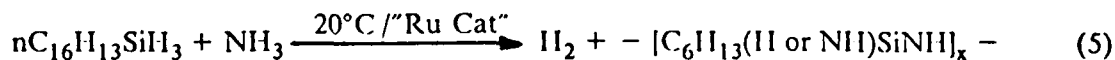
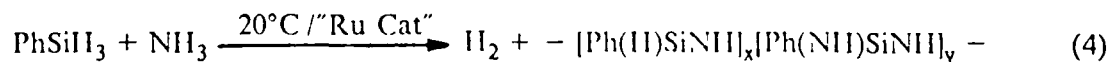
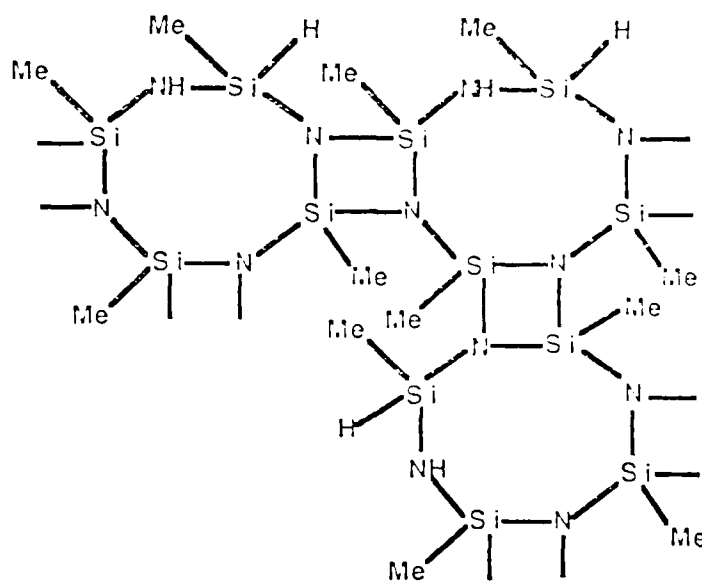


Table 2 contains the ceramic yields and compositions obtained from the pyrolysis of a set of Me(II)SiNH polysilazanes. Comparison of this data with the ceramic yield and composition obtained from pyrolysis of the MeHSiNH/MeSiN polysilazane prepared by Seyferth and Wiseman [4b, c], reaction (6), reveals no significant differences.

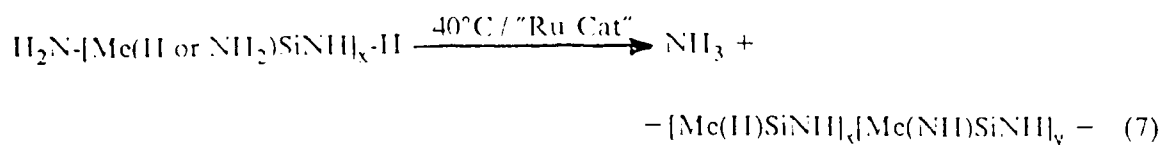
Table 2. Ceramic Yields and Apparent Ceramic Composition for a Series of Me(H)SiNH Polysilazanes Following Pyrolysis to 900°C under N₂ at a Heating Rate of 5°C/min.

Mol.Wt. (VPO,D)	Ceramic Yield %	C %	N %	H %	Si %	Si ₃ N ₄ %	SiC %	C %
351	19	18.28	23.63	1.00	57.51	59.2	31.4	8.8
546	32	17.04	25.88	0.93	56.02	64.8	24.3	9.8
1635	35	17.35	24.49	0.94	50.67	61.3	19.6	11.4
--	40	17.00	25.90	0.76	56.43	64.8	25.0	9.6
--	57	17.16	23.67	1.03	52.25	59.3	23.8	10.0

^aAll compositions are calculated based on the chemical analyses of the ceramic products. Because all the 900°C products are amorphous, the assigned values may not actually represent the true ceramic compositions.



The Me(H)SiNH polymers used to obtain the data in Table 2 were prepared first by reaction (1), which actually produces an oligomeric species of the type H₂N-[Me(H)SiNH]_x[Me(NH)_{0.5}SiNH]_y-H followed by heating in the presence of Ru₃(CO)₁₂ to promote chain growth and gelation via a condensation reaction of the type shown in reaction (7):



We have previously suggested [14, 16] that treating oligomeric polysilazanes containing Si-H bonds and N-H bonds with a ruthenium-based catalyst results in chain extension and gelation via dehydrocoupling reactions as exemplified by reaction (2). We now believe that reaction (7) may take precedence over reactions similar to (2) in the chain extension of this particular polymer [15].

Table 3 contains the ceramic yield and composition data resulting from the pyrolysis of a set of H_2SiNMe polysilazanes. Comparison of the MeHSiNH polysilazane pyrolysis results with those from the H_2SiNMe polysilazanes offers the novel opportunity to assess the effects of structural isomerism on ceramic yield and composition.

Table 3. Ceramic Yields and Apparent Ceramic Composition^a for a Series of H_2SiNMe Polysilazanes Following Pyrolysis to 900°C under N_2 at a Heating Rate of 0.5°C/min.

Mol.Wt. (GPC ^b ,D)	Ceramic Yield %	C %	N %	H %	Si %	Si_3N_4 %	N %	C %
800	40	18.89	35.44	0.88	45.18	75	5	19
1200	45-50	18.46	33.97	1.03	44.91	75	10	18
1700	39-45	19.09	35.87	0.83	43.64	73	7	19
2300	60-63	17.99	33.60	1.12	46.62	77	3	18

^aAll compositions are calculated based on the chemical analyses of the ceramic products. Because all the 900°C products are amorphous, the assigned values may not actually represent the true ceramic compositions.

^b M_N measured by gel permeation chromatography using polystyrene standards calibrated against VPO results.

The ceramic yields for polymers of about the same M_n are roughly the same for both isomers. Moreover, the major product in both instances is silicon nitride. The key differences arise in the other products formed. In the case of the H_2SiNMe polysilazane, we observe only the formation of excess carbon and nitrogen, whereas, the MeHSiNH polysilazane appears to form SiC and some excess carbon but no excess nitrogen (some hydrogen, approximately 1%, is also present in both systems).

The fact that SiC is observed in one system and not the other suggests that the SiC must form early in the decomposition process; otherwise, we would expect to observe its formation in both systems. That is, these results suggest that Si_3N_4 , or its amorphous precursor, may be resistant to reaction with free carbon during the pyrolysis process; otherwise, we would expect to observe the formation of SiC in the H_2SiNMe pyrolysis product. This conclusion again supports the conjecture that Si_3N_4 may be thermodynamically more stable than SiC under the pyrolysis conditions. Finally, the formation of SiC from pyrolysis of the MeHSiNH polysilazane

and not from pyrolysis of the H_2SiNMe polysilazane suggests that *SiC* must arise as a direct result of the Si-C bond in the MeHSiNH precursor.

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